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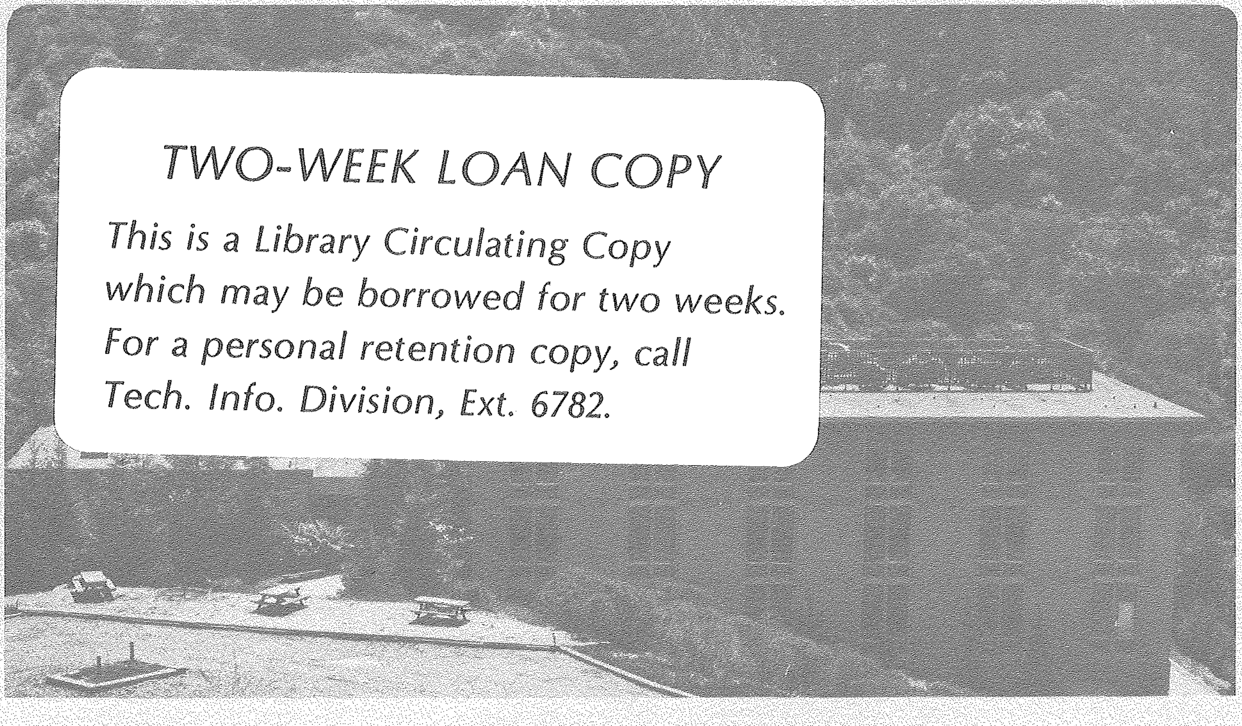

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Reaction and deactivation of HCl(v = 1, 2) by Cl, Br, and H atoms

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Total decay rates for HCl(v = 2, 1) were measured in the range 294 - 439 K for Cl, 295 - 390 K for Br, and at 296 K for H. HCl(v = 2) was produced directly by pulsed laser excitation of the overtone. The fraction of HCl(v = 2) relaxed to HCl(v = 1) was determined. For HCl(v = 2) + Cl, relaxation gave entirely HCl(v = 1) within an experimental uncertainty of ± 10%, the total relaxation rate was large, $k/\bar{v} \simeq 5\ \mathring{A}^2$, and rates varied only slightly with temperature. For Br + HCl(v = 2) reaction to HBr(v = 0) + Cl is exoergic by about kT. Relaxation to HCl(v = 1) is the dominant process. Reaction contributes roughly 17% and 34% to the loss of HCl(v = 2) at 295 and 390 K, respectively. In constrast to the result for Br and for O (reported previously) H + HCl(v = 2) gives 65% H_2 + Cl and only 35% HCl(v = 1) + H. For HCl(v = 1) + H, Cl, O the vibra-

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tional excitation energy is greater than the activation energy for reaction. The relaxation rates are between 1/2 and 1/3 of the A values for the measured thermal exchange rates $A \exp(-\Delta E_{act}/RT)$. For HCl($v = 1$) + Br, well below threshold, the rate is some 20 times less than for HCl($v = 1$) + Cl. The rate for HCl($v = 2$) + Br, just above reaction threshold is not dramatically larger. The ratios of vibrational relaxation rates for HCl($v = 2$) vs HCl($v = 1$) are 5.0 ± 1.3, 4.2 ± 0.4, and 5.0 ± 1.3 for O, Cl, and Br, respectively. Any first order linear perturbation treatment gives rates proportional to v; the data scale more closely as v^2.

I. INTRODUCTION

During the past decade a wide variety of information has been obtained on chemical reaction and vibrational relaxation in collisions between vibrationally excited molecules and reactive atoms.[1, 2] Many chemical reactions are greatly accelerated by vibrational excitation. Relaxation by reactive atoms proceeds orders of magnitude more rapidly than with inert collision partners. The purpose of this series of papers[3, 4] on HCl(v = 1, 2) is to explore the dependence of state-resolved relaxation and reaction rates upon quantum numbers. How do relaxation rates depend on vibrational quantum number; does the $\Delta v = \pm 1$ selection rule for vibration-to-translation and -rotation ($V \rightarrow T, R$) energy transfer apply to potentially reactive systems? How do rates change as the energy threshold for reaction is crossed? How do reaction and relaxation compete when both are possible?

As in previous experiments[4] on O + HCl, HCl is excited directly to $v = 2$ by a pulsed laser. By monitoring fluorescence as a function of time both from HCl($v = 2$) and from HCl($v = 1$) decay rates are measured for both levels and the fraction of HCl($v = 2$) relaxed to ($v = 1$) is determined. Thus in the system

$$\mathrm{Cl} + \mathrm{HCl}(v = 2) \rightarrow \mathrm{HCl}(v = 1) + \mathrm{Cl} \qquad (1)$$

$$\mathrm{Cl} + \mathrm{HCl}(v = 2) \rightarrow \mathrm{HCl}(v = 0) + \mathrm{Cl} \qquad (2)$$

$$\mathrm{HCl}(v = 2) + \mathrm{HCl}(v = 0) \rightarrow 2\mathrm{HCl}(v = 1) \qquad (3)$$

$$\mathrm{Cl} + \mathrm{HCl}(v = 1) \rightarrow \mathrm{HCl}(v = 0) + \mathrm{Cl} \qquad (4)$$

it is possible to measure $k_1 + k_2$, k_4 and $k_1/(k_1 + k_2)$. Process

(3) is eliminated by extrapolation to $P_{HCl}/P_{Cl} = 0$. Thus the dependence of relaxation rate on quantum number and the importance of $\Delta v = 2$ compared to $\Delta v = 1$ are determined.

The quasiclassical trajectory calculations of Smith and others give relaxation primarily in collisions which cross, or cross and recross, the barrier to reaction.[1] Recently Kneba and Wolfrum[5] have shown that the isotope exchange reaction rate for HCl($v = 1$) is twice the vibrational relaxation rate. Since exothermic reactions give broad vibrational distributions in products, the same might be expected for "reactive" relaxation processes. Furthermore, calculated relaxation rates for collisions energetically below the reaction threshold are negligibly small. For the endothermic reaction system

$$\mathrm{Br} + \mathrm{HCl}(v = 0) \rightarrow \mathrm{HBr} + \mathrm{Cl} \quad \Delta H^{o}_{o} = 5490\ \mathrm{cm}^{-1} \tag{5}$$

the calculated rate is much less than that measured for HCl($v = 1$) but of the correct order of magnitude for $v = 2$.[6] For reaction (5) the previously available rate data for forward and reverse reactions do not satisfy the principle of microscopic reversibility.[1, 3, 7] Earlier measurements on HCl($v = 2$) + Br are extended here.[3]

The kinetics of H + HCl, for both abstraction

$$\mathrm{H} + \mathrm{HCl}(v = 0) \rightarrow \mathrm{H}_2(v = 0) + \mathrm{Cl} \quad \Delta H^{o}_{o} = 359\ \mathrm{cm}^{-1} \tag{6}$$

and exchange reactions have been studied for many years.[8] Here we add to the growing, albeit confusing, store of knowledge the rates for relaxation and reaction of HCl($v = 2$) by H.

II. EXPERIMENTAL

The basic experimental apparatus has been described in detail in several previous publications. The apparatus configuration of Ref. 4 was used. A small oven was added around the flow tube, downstream from the titration zone, extending 12 cm on either side of the observation port. Two calibrated iron-constantan thermocouples were inserted into the gas flow through pyrex sleeves 5 cm on either side of the observation port. The thermocouple voltages were read with a Newport digital microvoltmeter. Heated air, at the same temperature as the oven, was blown over the observation port windows to reduce window cooling. The oven was turned on for at least an hour before a run; its temperature remained stable within 3 K. Both thermocouples gave the same oven temperature before the gas flows were started. However, with gas flowing the upstream thermocouple consistently gave a lower temperature reading by ~ 5 K than the downstream one. The gas temperature was taken as the downstream reading. The maximum temperature was limited by the ir detector noise caused by background thermal emission from the hot oven. For temperatures above ambient, an iris above the fluorescence window limited the detector field of view to the center of the fluorescence region. The background was further limited by replacing the cooled 3 - 5 μ interference filter by a 3 - 4 μ filter. The transmission of this filter was about 4% less for the 2 → 1 fluorescence band than for the 1 → 0.

The production and titration of Cl and Br atoms was carried out as before. H atoms were produced by a microwave discharge in either pure H_2 (Matheson 99.999 %) or H_2 diluted by Ar or He. The H atom concentration was determined by gas phase titration using NOCl.[9] The intensity of the chemiluminescence from HNO, I^*, was monitored as a function of the flow rate of added NOCl, f_{NOCl}. Titration plots of I^*/f_{NOCl} vs f_{NOCl} were linear and were extrapolated to determine the end point of the titration to better than ± 10%. Titration of the H atoms was carried out close enough to the observation port, 10 cm, that < 5% of the atoms were lost at the 10 - 12 m/sec flow velocities used in this work. Since H atom concentration could not be monitored by a recombination afterglow, the titration was carried out several times during an experimental run. In most cases P_H varied by only a few percent. For the final experimental run the H atoms were also titrated using NO_2 as the titrant gas[10] as well as NOCl. The end point for the NO_2 titration was reached when the chemiluminescence from the flow tube was extinguished. Although great care must be used in interpreting the NO_2 + H titration reaction,[10] the H atom flow obtained using a stoichiometry of 1.5 was only 10% greater than that measured using NOCl as the titrant gas. Because of the unfavorable ratio of P_H/P_{H_2} in the other runs, this was the only experiment in which both NO_2 and NOCl titrations were carried out.

III. RESULTS AND ANALYSIS

The kinetic scheme, rate equations and data analysis have been described in detail for the HCl + O system.[4] The data for HCl(v = 2) + Cl, Br, and H are analyzed in the same way. The decay rate, K_{21}, for v = 2 → 1 fluorescence as a function of reactive atom concentration gives the total rate constant, $k_T^{2,R}$, for removal of v = 2 molecules by reactive atoms, R. The slower decay rate, K_{10}, of v = 1 is deduced from the total fluorescence by a double exponential analysis in which the fast rate is constrained to match K_{21} within ± 15%.

The relative amplitude of 1 → 0 to 2 → 1 emission intensity, I_1/I_2, gives the fraction of v = 2 molecules which appear in v = 1, $k_{\Delta v=1}^{2,R}/k_T^{2,R}$. The effect of V → V energy transfer process (3) is removed by extrapolation to zero HCl pressure. Thus the quantity

$$M \equiv \frac{I_1}{I_2} \; \frac{A_{21}}{A_{10}} \left(\frac{K_{21}-K_{10}}{[R]}\right) \approx 2k_3 \; \frac{[HCl]}{[R]} + k_{\Delta v=1}^{2,R}$$

plotted vs. P_{HCl}/P_R has a slope $2k_3$ and intercept $k_{\Delta v=1}^{2,R}$. Systematically small values of I_1/I_2 result from self-absorption at high HCl pressure. Measurement of I_1/I_2 without atoms for T = 295 K for P_{HCl} = 0.1 torr gave roughly a 5% decrease from the expected value of 1.06. The effect is negligible for the room temperature results and is significantly less than other uncertainties for the lowest P_{HCl}/P_R values which fix the intercept.

A. HCl + Cl

The experimental conditions for decay time measurements and results for the determination of k_4 and $k_T^{2,Cl} = k_1 + k_2$ as a function of temperature are summarized in Table I. At least 3 independent experimental runs were carried out for each temperature. As well, for each combination of HCl and atom pressure, in each run, at least 2 fluorescence curves were recorded and the results averaged. The uncertainties listed in Table I are standard deviations for a single measurement from the mean of each data set. The relative intensity data are plotted as M vs P_{HCl}/P_{Cl} in Figs. 1 and 2. For the room temperature data the slope in Fig. 1 was fixed at $2k_3$, with the well-established value[11] of $k_3 = 1.0 \times 10^5$ sec^{-1} $torr^{-1}$. For higher temperatures the data points were fit by a least squares straight line. The slope values in Table II are equal to within experimental uncertainties to twice the k_3 values given in Table I. The intercepts give k_1 values which are within 10% of the $k_T^{2,Cl} = k_1 + k_2$. The values of k_2/k_1 are independent of errors in the Cl atom pressure. The uncertainties are estimated as one-half the extreme limits of intercepts in Figs. 1 and 2 plus an additional 0.05 for uncertainty in $A_{21}/A_{10} = 1.88$ and systematic error in the measurement of I_1/I_2. Since all of the values of k_2/k_1 are less than 10% and within experimental error of zero, the contribution of two-quantum transfer, process (2), to the deactivation of v = 2 is less than 10% and possibly much smaller.

B. HCl + Br

The complete reaction and relaxation scheme for HCl($v = 2$) + Br has been presented in detail.[3] Here we are concerned with the reaction sequence:

$$\mathrm{Br} + \mathrm{HCl}(v = 2) \rightarrow \mathrm{HBr}(v = 0) + \mathrm{Cl} \quad (7)$$

$$\mathrm{Br} + \mathrm{HCl}(v = 2) \rightarrow \mathrm{HCl}(v = 1) + \mathrm{Br} \quad (8)$$

$$\mathrm{Br} + \mathrm{HCl}(v = 2) \rightarrow \mathrm{HCl}(v = 0) + \mathrm{Br} \quad (9)$$

$$\mathrm{Br} + \mathrm{HCl}(v = 1) \rightarrow \mathrm{HCl}(v = 0) + \mathrm{Br} \quad (10)$$

Cl atoms produced in (7) are converted back to Br atoms on every second or third collision with Br_2.

$$\mathrm{Cl} + \mathrm{Br}_2 \rightarrow \mathrm{ClBr} + \mathrm{Br} \quad (11)$$

E → V transfer processes yielding $Br(^2P_{1/2})$ are implicitly included in (8) - (10); arguments in Ref. 3 show that their contribution is small.

The data are collected and analyzed in a manner completely analogous to that described for Cl atoms. The results are given in Tables III and IV and in Figs. 3 and 4. The data at 391 K are identical in form to those at 355 K. Because the rate constants for Br atoms are ten to twenty times smaller than those for Cl, the extrapolations in Figs. 3 and 4 are longer than those in Figs. 1 and 2. Consequently, the intercepts and thus the fraction of $v = 2$ molecules which reach $v = 1$ is less accurately determined. The slopes in Figs. 3 and 4 and in Table IV are determined from least-squares fits to the data. They are 5 to 15% less than the $2k_3$ values determined

directly from decay time measurements. If the slopes were constrained to the later values, the k_8 values would be decreased by about the same percentage. The values of k_{10} for $v = 1$ relaxation are very poorly determined since HCl($v = 1$) molecules often flowed out of the observation zone more rapidly than they were relaxed by Br. Earlier measurements of k_{10} are more accurate (Sec. IV-C).

C. HCl + H

H atom may react chemically with ground state HCl, Eq. (6), as well as with vibrationally excited HCl. For HCl(v = 2, 1) the possible reaction and relaxation processes are:

$$H + HCl(v = 2) \rightarrow H_2(v = 1, 0) + Cl \qquad (12)$$

$$H + HCl(v = 2) \rightarrow HCl(v = 1) + H \qquad (13)$$

$$H + HCl(v = 2) \rightarrow HCl(v = 0) + H \qquad (14)$$

$$H + HCl(v = 1) \rightarrow H_2(v = 0) + Cl \qquad (15)$$

$$H + HCl(v = 1) \rightarrow HCl(v = 0) + H \qquad (16)$$

The decay times of emission from v = 2 and v = 1 give the rates $k_T^{2,H} = k_{12} + k_{13} + k_{14}$ and $k_T^{1,H} = k_{15} + k_{16}$ as shown in Table V. The errors given for each run are the standard deviations of the data set for that run. The error margins for the average values are outer limits for all possible sources of error. Gross systematic error in the H atom titration is not likely.

The production of Cl atoms by Rx(6) is a possible source of systematic error. At equilibrium $P_{Cl}/P_H = K_6(P_{HCl}/P_{H_2}) = 3.4\ (P_{HCl}/P_{H_2})$. The largest value, $P_{HCl}/P_{H_2} = 0.082$, applies to the highest HCl pressure in the last run in Table V. For that case at equilibrium $P_{Cl}/P_H = 0.28$. The Cl atom pressure approaches the equilibrium limit with a rate given by $k_6P_{HCl} + k_{-6}P_{H_2} = 200\ sec^{-1}$. At the flow rate of 10 - 12 m/sec the HCl reaches the excitation zone 2 - 2.5 msec after injection. The HCl relaxation times are a fraction of a msec. Under these conditions P_{Cl} reaches 36% of its equilibrium

value; thus only 8% of H atoms are converted to Cl atoms in this single worst case. Using the rate constants from Tables I and V the observed rates are systematically increased by the conversions of H atoms to Cl atoms by 2% for $v = 2$ and by 9% for $v = 1$. The effect is insignificant in this and all other cases.

The relative intensity data plotted in Fig. 5 show values of M calculated for each decay curve from the decay constants for that particular curve, $M = [K_{21} - K_{10}]/P_H$. Only curves which could be analyzed accurately as double exponentials were used. Agreement of the fast decay rate with that determined for $v = 2$ fluorescence alone was better than 10%. When best values of k_i's and measured pressures are used to calculate $[K_{21} - K_{10}]$, as for Figs. 1 - 4, slope and intercept were obtained. Less than half (35 ± 15%) the loss of HCl($v = 2$) by collisions with H yields HCl($v = 1$), Table VI. Because the reaction rate is a substantial fraction of the total, its magnitude is much more accurately determined than that for Br or O atoms.

IV. PREVIOUS EXPERIMENTAL RESULTS

A. HCl + HCl

At 296 K Leone and Moore[11] have measured k_3 to be $(3.1 \pm 0.34) \times 10^{-12}$ cm^3 molecule^{-1} sec^{-1} by directly exciting HCl(v = 0) to HCl(v = 2). Noter et al.[12] have measured the reverse of Reaction (3) from 300 K to 700 K. An analysis of their data gives k_3 to be 2.5×10^{-12} cm^3 molecule^{-1} sec^{-1} at 300 K and 1.9×10^{-12} cm^3 molecule^{-1} sec^{-1} at 400 K. The present results for k_3, Tables I and III, are in agreement with these measurements over the limited temperature range of the experiments, 294 K to 439 K.

B. HCl + Cl

There have been five different measurements of k_4 near 300 K. At 294 K Macdonald et al.[13] have reported the average value of k_4 from two different techniques to be $(8.8 \pm 2.6) \times 10^{-12}$ cm^3 molecule^{-1} sec^{-1} in good agreement with earlier results.[14] Brown et al.[15] have measured k_4 over the temperature range 195 K to 400 K. At 299 K they find k_4 to be 9.3×10^{-12} cm^3 molecule^{-1} sec^{-1}. Karny and Katz[16] have also measured k_4 at room temperature to be $(7.0 \pm 1.5) \times 10^{-12}$ cm^3 molecule^{-1} sec^{-1}. Recently Kneba and Wolfrum[5] and earlier Arnoldi and Wolfrum have found $k_4 = (6.1 \pm 1.3) \times 10^{-12}$ at 298 K. All of these measurements are in good agreement with each other as well as with the results of this work, Table I, at 294 K.

Brown et al.[15] have measured k_4 over the temperature range 195 K to 400 K. At 400 K they find k_4 to be 1.5×10^{-11} cm^3 $moelcule^{-1}$ sec^{-1} a factor of about 2 greater than the value measured here, Table I. This disagreement is larger than one might expect since at 300 K their value of k_4 is only 20% greater than the present measurement, Table I. However, this disagreement is probably within the systematic errors inherent in the different methods of Cl atom production and determination as well as the different techniques for producing HCl(v = 1). The smaller value of k_4 at 400 K might be preferred due to the more direct method of Cl atom production in the present work as well as the smaller perturbation of the system by the direct laser excitation from HCl(v = 0) to (v = 2) and subsequent relaxation to HCl(v = 1).

Ridley and Smith[17] have measured the total deactivation rate constant for HCl(v = 1), HCl(v = 2), and HCl(v = 3) by Cl atoms by producing vibrationally excited HCl in a chemical reaction in an excess of Cl atoms. Although their absolute value of k_4 is incorrect there is reason to believe[13, 15] that the relative values of the deactivation rate constants are correct. They determined $k_T^{2,Cl}/k_4 \simeq 3.2$ in reasonable agreement with the value, 4.4 ± 0.8, Table I.

C. HCl + Br

Several groups have measured k_{10}. At 295 K Leone et al.[3] have found k_{10} = (2.8 ± 0.5) x 10^{-13} cm^3 $molecule^{-1}$ sec^{-1}. With similar techniques Arnoldi et al.[7, 18] and Karny and Katz[16] found k_{10} = (2.8 ± 0.7) x 10^{-13} and (2.6 ± 0.5) x 10^{-13} cm^3 $molecule^{-1}$ sec^{-1}, respectively at 295 K. Brown et al.[6] have measured k_{10} from 210 K to 371 K. At 296 K they find k_{10} = (4.8 ± 0.9) x 10^{-13} cm^3 $molecule^{-1}$ sec^{-1}, a factor of 1.8 greater than other measurements. They produced Br atoms from reaction of a measured concentration of O atoms with Br_2. Arnoldi and Wolfrum[7] found k_{10} = (3.4 ± 1.0) x 10^{-13} cm^3 $molecule^{-1}$ sec^{-1} using the same method. Karny and Katz[16] have suggested that the presence of BrO may accelerate the deactivation of HCl(v = 1). The present experiments were not designed to measure rates as slow as k_{10}. The values of k_{10} in Table III are consistent with the earlier and more precise values.[3, 7, 16]

Previously Leone et al.[3] have reported $k_T^{2,Br}$ to be (1.8 ± 0.3) x 10^{-12} cm^3 $molecule^{-1}$ sec^{-1} at 295 K. These experiments were carried out exactly analogously to those reported here. However, the use of an intracavity etalon and placement of the OPO in the same room as the flow apparatus greatly improved the signal-to-noise ratio of the observed ir fluorescence in the present experiments. This has allowed work with P_{HCl} as low as 8 mtorr there by reducing the contribution of

k_3P_{HCl} to the total deactivation rate of HCl(v = 2) and decreasing the scatter in the measurement of $k_T^{2,Br}$. The results of these two determinations are in excellent agreement.

Arnoldi and Wolfrum[7] have measured k_7 to be (1.5 ± 1.0) x 10^{-12} cm^3 $molecule^{-1}$ sec^{-1} at 295 K but not $k_T^{2,Br}$. At 295 K we find k_7 to be (3 ± 3) x 10^{-13} cm^3 $molecule^{-1}$ sec^{-1}, Table IV. Arnoldi and Wolfrum[7] produced HCl(v = 2) by sequential absorption of the 1 → 0 and 2 → 1 emission from an HCl chemical laser and measured k_7 by mass spectrometric detection of BrCl on time scales long compared to the relaxation and reaction processes. The direct excitation of HCl(v = 0) to (v = 2) and subsequent monitoring of the infrared fluorescence to estimate the partitioning between relaxation and reaction used in our study should not be complicated by any large experimental artifacts. While this technique cannot give highly accurate values for the partitioning, the more direct nature of the experimental measurement should be preferred. Although the reported values differ by a factor of five, it should be noted that the error ranges do in fact overlap.

Douglas et al.[19, 20] have measured the relative reaction rate constants for HCl(v = 1 - 4) + Br atoms at approximately 300 - 400 K, using a chemiluminescence depletion technique. They estimated that k_7 is between 5 x 10^{-13} and 2 x 10^{-12} cm^3 $molecule^{-1}$ sec^{-1} and that for HCl(v = 2) k_7 was 3 times greater than k_8. In contrast Table IV gives k_7 = (3 ± 3) x 10^{-13} cm^3 $molecule^{-1}$ sec^{-1} at 295 K, only about one fifth of k_8.

At 390 K k_7 increases to one half of k_8. It may be possible to reconcile these observations if one considers the dependence of rate constants on rotational state and the differences in rotational distributions for the two experiments.

For the reaction Cl + HI → HCl + I the dependence of rate on temperature, isotopic substitution and relative translational energy suggests that HI rotation is involved in the reaction coordinate and that reaction rate increases with rotational energy.[21] A similar effect can be expected for the Cl + HBr reaction and its reverse k_7. The rates reported by Douglas et al.[19, 20] are arithmetic averages over the rates for $J = 0$ through 8. Thus their k's are for higher rotational energies than a 300 K Boltzmann distribution. Contrary to the above suggestion that reaction rates may increase with rotational quantum number, Douglas et al.[20] point out that higher J levels are less depleted and thus react less rapidly. An alternative explanation of this result is that vibrational relaxation $v \rightarrow v - 1$ produces molecules with high rotational and translational energies. Translationally hot molecules pass through the white cell more rapidly and hence their fluorescence is detected less efficiently. They appear to have been chemically depleted. Higher J states with less translational energy fluoresce with higher efficiency thus causing an apparent decrease in the chemical depletion of these levels. Thus two effects, increased reaction rate for higher rotational energies and counting relaxation as reaction may be responsible for

the difference in reported k_7/k_8 values. These effects are most severe for reaction (7) since it is occuring near threshold.

D. HCl + H

There have been several determinations of $k_T^{1,H}$. At 295 K Arnoldi and Wolfrum[7] report a value of (7.0 ± 1.0) x 10^{-12} cm^3 $molecule^{-1}$ sec^{-1} in agreement with the value of (7.6 ± 2.3) x 10^{-12} cm^3 $molecule^{-1}$ sec^{-1} found by Bott and Heidner.[22] The value of $k_T^{1,H}$ reported in Table VI is a factor of 2 smaller. As for k_{10}, $k_T^{1,H}$ is poorly determined because at the low partial pressure of H atoms it makes only a small contribution to the total removal of HCl(v = 1). The earlier values of $k_T^{1,H}$ are taken to be correct.

There have been no previous measurements of the removal of HCl(v = 2) by H atoms.

V. DISCUSSION

Several qualitatively interesting features emerge from the data in Tables I - VI. For Cl + HCl(v = 2) vibrational relaxation yields HCl(v = 1) and not HCl(v = 0). Thus at least for this potentially reactive system multiquantum transfers are unimportant. For Br + HCl(v = 2) collisions, relaxation is faster than exchange, Table II, last column. The exchange reaction is just at threshold with respect to total energy. Because most HCl(v = 2) molecules relax to HCl(v = 1) this rate constant is determined with good accuracy. Table VII shows the ratios of these rates to those for relaxation of HCl(v = 1). For the reactive atoms Cl, Br, and O for which good data are available, HCl(v = 2) relaxes 4 or 5 times more rapidly than HCl(v = 1). In fact these rates appear roughly proportional to v^2, whereas v^1 is expected for any linear first order perturbation theory of vibrational relaxation. Some data on HF and DF support a similar conclusion.[23] For collisions of HCl(v = 2) with H reaction dominates and accurate relaxation data are not obtained.

For systems with activation energies less than the vibrational quantum, 8 kcal/mole, the relaxation rates correlate well with the A factor for the thermal reaction, Table VII. For H, O, and Cl the HCl(v = 1) relaxation rates are about one third of the corresponding A factors. For Br + HCl(v = 1) with an activation energy double for vibrational quantum energy, the $k_{v = 1}$ is 20 times less than for Cl + HCl(v = 1).

A. HCl + Cl

A collision between a $Cl(^2P_u)$ atom and an $HCl(^1\Sigma^+)$ molecule can occur on 3 possible potential hypersurfaces, $^2A'$ and $^2A''$ correlating to $Cl(^2P_{3/2})$ and $^2A'$ correlating to $Cl(^2P_{1/2})$ under general C_s symmetry. Nikitin and Umanski[24] have shown that it is possible to obtain vibrational relaxation in multi-surfaced atom-diatom systems due to non-adiabatic transitions between the vibronic surfaces of the atom-molecule system. The spin-orbit interaction is expected to be the largest term coupling the adiabatic vibronic states. It is also expected that the relaxation rate constants for different vibrational levels, v, should scale as v with $\Delta v = 1$ processes dominating.

The experimental evidence[5, 15, 17, 25] does not seem to support the non-adiabatic vibronic curve crossing mechanism for vibrational relaxation of HCl(v) by Cl atoms. The dependence of rate on quantum number is strongly nonlinear, roughly quadratic (Table VII). Kneba and Wolfrum[5] have measured the rate constant for the process

$$Cl(^2P_{3/2}) + HCl(v = 1) \rightarrow HCl(v = 0) + Cl(^2P_{1/2}) \qquad (18)$$

at 298 K to be ~ 100 times smaller than k_4. Thus a major non-adiabatic coupling mechanism in Nikitin's theory is 2 orders of magnitude too small to explain the experimental rate constants. Finally, the observed decrease in k_4 on D atom substitution indicates that non-adiabatic curve crossing is not the largest relaxation channel.[25]

For the Cl + HCl(v) system it appears that the dynamics are dominated by one potential hypersurface. This surface must reflect the possibility for "chemical reaction." The exchange reaction

$$Cl' + HCl''(v) \rightarrow HCl'(v') + Cl'' \qquad (19)$$

may be vibrationally non-adiabatic. Recently, Kneba and Wolfrum[5] have measured the rate k_{20} at 298 K to be twice

$$^{37}Cl + H^{35}Cl(v = 1) \rightarrow H^{37}Cl(v = 0, 1) + {}^{35}Cl \qquad (20)$$

k_4 and a factor of 10^3 greater than the $H^{35}Cl(v = 0)$ rate constant. The barrier height determined experimentally[5] for the thermal, HCl(v = 0) + Cl, exchange reaction appears to be 6.6 ± 0.5 kcal/mole. Smith and Wood[26] and Smith[27] have investigated vibrational relaxation in atom-exchange reactions using quasi-classical trajectory calculations. For the Cl + HCl(v = 1) system the trajectory calculations of Smith[27] are in reasonable agreement with experimentally measured rate processes for an LEPS potential hypersurface only when the barrier to exchange is reduced to 1.89 kcal/mole. Smith and Wood[26] and Smith[27] found that relaxation was likely only if the collision reached a configuration of equal bond extensions for reagents and products. Model quasi-classical trajectory calculations have shown that the dynamics of atom-diatom collisions can be quite sensitive to the fine features of the topology of the potential hypersurface. Thus curvature of the minimum energy path,[28] the nature of slope that leads up

to the barrier crest[29] and the form of the inner repulsive wall[28, 30] as well as gross features such as location and height of the barrier[31] must be carefully considered in order to compare the results of trajectory calculations to experimental rate constants.

B. HCl + Br

Similar arguments also apply to relaxations of HCl(v) by Br. There have been several[20, 32, 33] quasi-classical trajectory studies of this reaction. In general, these calculations are roughly in agreement with experimental trends for HCl(v = 2). We have suggested that the rapid increase in k_7 with increasing temperature is due to an increase of reaction rate with rotational energy. Douglas et al.[20] used a 300 K translational distribution and a 600 K rotational distribution for the reagent HCl(v) in their calculations. For HCl(v = 2), reaction and relaxation processes were calculated to be equally likely. Smith[32] determined that vibrational energy transfer was most likely to occur in collisions where the configuration $(r_{HBr}/r_{eHBr}) = (r_{HCl}/r_{eHCl})$ was reached. It seems probable that small changes in the topology of the potential hypersurface in this region could lead to large variations in calculated energy transfer and reaction rates. Smith calculated a negligible rate for relaxation of HCl(v = 1) by Br at 298 K. No relaxation occured unless sufficient energy was available for reaction to occur as well. Smith concluded that non-adiabatic transfer probably accounts for k_{10}. In view of the

arguments above for HCl + Cl which are equally valid for HCl + Br, it may be that a change in potential surface shape is indicated instead. Perhaps the reaction coordinate is more strongly curved in the region accessible to HCl(v = 1) + Br.

The measured rate of reaction (7) may be compared to that of the reverse reaction,[1, 3, 7]

$$\mathrm{Cl} + \mathrm{HBr}(v = 0) \xrightarrow{k_{-7}} \mathrm{HCl}(v = 2) + \mathrm{Br}.$$

The total reaction rate for Cl + HBr is accurately known, $(8.4 \pm 0.5) \times 10^{-12}\ \mathrm{cm}^3\ \mathrm{molecule}^{-1}\ \mathrm{sec}^{-1}$.[21] The relative product yield HCl(v = 2)/HCl(v = 1) has recently been determined[34] to be 0.12 ± 0.03. An earlier result[35] based on a single preliminary measurement was 0.4. The ratio HCl(v = 1)/HCl(v = 0) can only be set between 0 and 1.[3] The rate k_{-7} is established within the range $(8 \pm 4) \times 10^{-13}\ \mathrm{cm}^3\ \mathrm{molecule}^{-1}\ \mathrm{sec}^{-1}$. From microscopic reversibility k_7 must be given by[1]

$$k_7 = k_{-7} \left(\frac{\mu}{\mu'}\right) \left(\frac{B'}{B}\right) e^{\Delta\varepsilon/kT}$$

where μ and μ' are the reduced masses for collisions Cl + HBr and Br + HCl respectively, B' and B are the rotational constants for HCl(v = 2) and HBr(v = 0) and $\Delta\varepsilon = 190 \pm 40\ \mathrm{cm}^{-1}$ is the exoergicity of reaction (7). This equation must hold as long as k_7 and k_{-7} are measured with <u>reagents</u> at rotational and translation thermal equilibrium. Thus k_7 is calculated in the range $(2.2 \pm 1.8) \times 10^{-12}\ \mathrm{cm}^3\ \mathrm{molecule}^{-1}\ \mathrm{sec}^{-1}$ at 295 K. Experimentally (Tables III and IV), the total inelastic rate is $k_T^{2,\mathrm{Br}} = (1.7 \pm 0.2) \times 10^{-12}\ \mathrm{cm}^3\ \mathrm{molecule}^{-1}\ \mathrm{sec}^{-1}$ and the

reactive part is $k_7 = (0.3 \pm 0.3) \times 10^{-12}$ cm^3 molecule^{-1} sec^{-1}. The measured and calculated ranges for k_7 are very wide but even so just barely overlap. If we use the accurately measured $k_T^{2,Br}$ as an upper limit on k_7 and combine this with the accurate value for the total reaction rate of Cl + HBr, the maximum fraction of HCl(v = 2) product from Cl + HBr would be 0.07. This clearly rules out the earlier[35] HCl(v = 2)/HCl)v = 1) measurement. More accurate measurements of the product distribution for Cl + HBr including HCl(v = 0) and of $k_7/k_T^{2,Br}$ are required for a useful comparison with microscopic reversibility.

C. HCl + H

The reaction of an H(^2S_g) atom with an HCl($^1\Sigma^+$) molecule can take place on only a single $^2A'$ potential hypersurface. However, there are two "reactive" channels energetically allowed: (a) the abstraction reaction

$$H + HCl \rightarrow H_2 + Cl \qquad (21)$$

or (b) the exchange reaction:

$$H' + H''Cl \rightarrow H'Cl + H'' \qquad (22)$$

These reactions have been extensively studied under thermal, molecular beams, and laser excitation conditions. Potential surfaces have been calculated and classical trajectory studies carried out. References 8 and 36 discuss this work in detail. The activation energy for the thermal abstraction reaction has been found to be 3.2 - 3.6 kcal/mole and at 298 K k_{21} has

been measured to be 4 x 10^{-14} cm^3 $molecule^{-1}$ sec^{-1}.[8] Values for the activation energy of the exchange reaction range from 6 to 20 kcal/mole.

Both the abstraction and exchange reactions have been investigated[7] for HCl(v = 1). For the reaction

$$H + HCl(v = 1) \xrightarrow{k_{23}} H_2 + Cl \qquad (23)$$

at 295 K Arnoldi and Wolfrum[7] found that k_{23} was less than 1.3 x 10^{-13} cm^3 $molecule^{-1}$ sec^{-1}. This is only 2% of the total removal rate constant for HCl(v = 1) by H atoms. They reported[2, 7] that

$$D + HCl(v = 1) \xrightarrow{k_{24}} DCl(v = 1, 0) + H \qquad (24)$$

accounts for 10% of the total removal rate of HCl(v = 1) by D atoms and that at 298 K k_{24} is 8.3 x 10^{-13} cm^3 $molecule^{-1}$ sec^{-1}.

For HCl(v = 2) + H abstraction (12) is the major loss channel, 65 ± 15%. Relaxation (13) to HCl(v = 1) is somewhat less probable. No information on the exchange process can be obtained. The increase in abstraction rate with vibrational excitation is dramatic for HCl(v = 2):

$$k^{abs}_{v=2}/k^{abs}_{v=0} = k_{12}/k_{21} = 430 \pm 65.$$

However, for HCl(v = 1), $k_{23}/k_{21} < 4.2$, there is little, if any, effect.[2, 7] Both HCl(v = 1) and HCl(v = 2) are substantially above the activation barrier for abstraction. In the case of H + HF(v) rates are dramatically larger for

the first level, v = 3, above the barrier to abstraction. Total loss rates of HF(v) in collisions with H are 2.3, 10, and 1000 x 10^{-13} cm^3 $molecule^{-1}$ sec^{-1} for v = 1, 2, and 3, respectively.[37] The rate of abstraction for HCl(v = 1) + H seems slow by comparison.

The H + HCl(v) system appears to be an ideal dynamical system for future study. All three sources of reagent energy, translation, rotation, and vibration, appear to dramatically influence the dynamics of this reactive system. It appears possible that an accurate *ab initio* potential hypersurface could be produced and used to calculate rate constants and cross sections.

VII. ACKNOWLEDGMENTS

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TABLE I. HCl(v = 2, 1) + Cl - experimental conditions and rate constants derived from decay times.

T	P_{Ar}	P_{Cl_2}	P_{HCl}	P_{Cl}	k_4	$k_T^{2,Cl}$	k_3 [a]
(K)	(torr)		(mtorr)			(cm^3 molecule^{-1} sec^{-1} x 10^{12})	
294	2.35 - 3.20	82 - 170	15 - 110	35 - 107	7.4 ± 0.5	33 ± 4	3.1 ± 0.5
350 [b]	2.59 - 2.67	100	45 - 140	89 - 90	7.6 ± 0.7	36 ± 4	3.2 ± 0.5
381	1.91 - 3.25	58 - 130	38 - 150	27 - 100	9.9 ± 1.5	38 ± 2	3.2 ± 0.5
411	3.14 - 3.23	99 - 130	38 - 130	27 - 90	7.6 ± 0.7	37 ± 4	2.7 ± 0.4
439	2.67	61 - 90	130 - 170	85 - 125	8.1 ± 0.8	32 ± 4	2.3 ± 0.4

a. From values of K_{21} with P_{Cl} = 0.

b. Only one experimental run.

TABLE II. $HCl(v = 2, 1) + Cl$ - data derived from amplitude ratios.[a]

T	Slope	k_1[b]	k_2[c]	$\frac{k_2}{k_T^{2,Cl}}$[c]
°K	(cm^3 molecule^{-1} sec^{-1} x 10^{12})			
294	6.2[d]	32 ± 8	1 ± 3	0.03 ± 0.1
381	6.5	34 ± 7	4 ± 4	0.10 ± 0.1
411	7.0	37 ± 10	0 ± 3	0.00 ± 0.1

a. From data of Figs. 1 and 2.

b. Intercept of M vs P_{HCl}/P_{Cl}.

c. k_2 is $k_T^{2,Cl}$ from Table I minus k_1 from Table II.

d. Fixed at $2k_3$ value from Ref. 11.

TABLE III. HCl(v = 2, 1) + Br - experimental conditions and rate constant derived from decay times.

T	P_{Ar}	P_{Br_2}	P_{HCl}	P_{Br}	k_{10}	$k_T^{2,Br}$	k_3
(K)	(torr)	(mtorr)			(cm^3 $molecule^{-1}$ sec^{-1} x 10^{12})		
295	2.30 - 2.93	77 - 87	8 - 30	66 - 86	0.33 ± 0.18[a]	1.7 ± 0.1	4.0 ± 0.6
355	1.90 - 2.85	37 - 140	38 - 130	78 - 120	0.25 ± 0.07	2.4 ± 0.3	3.3 ± 0.3
390	2.88 - 2.96	33 - 70	38 - 120	73 - 103	0.38 ± 0.16	3.3 ± 0.5	3.3 ± 0.5

[a] The value (2.8 ± 0.5) x 10^{-13} cm^3 $molecule^{-1}$ sec^{-1} Refs. 3, 7, and 16 should be used.

TABLE IV. $HCl(v = 2, 1) + Br$ - data derived from amplitude ratios.[a]

T	Slope	k_8[b]	k_7[c]	$\frac{k_7}{k_T^{2,Br}}$
°K	(cm^3 molecule^{-1} sec^{-1} x 10^{12})			
295	5.9	1.4 ± 0.4	0.3 ± 0.3	0.17 ± 0.15
355	5.4	2.0 ± 0.6	0.4 ± 0.35	0.18 ± 0.12
390	5.6	2.2 ± 0.6	1.1 ± 0.6	0.34 ± 0.13

a. From data in Figs. 3 and 4.

b. Intercept of M vs P_{HCl}/P_{Br}.

c. k_7 is $k_T^{2,Br}$ from Table III minus k_8 from Table IV; it is assumed that $k_6 = 0$.

TABLE V. HCl(v = 2, 1) + H - experimental conditions and rate constants derived from decay times at 296 ± 1 K.

M	P_M	P_{H_2}	P_{HCl}	P_H	$k_T^{1,H\,a}$	$k_T^{2,H}$
	(torr)		(mtorr)		(cm^3 molecule^{-1} sec^{-1} x 10^{12})	
-	-	3.36	8 - 34	16 - 21	3.7	29 ± 1
-	-	3.45	6 - 37	12	3.9	28 ± 2
He	3.48	0.39	17 - 32	41	3.1	22 ± 4
average values					3.4	26 ± 5

a. Ill-defined; see Sec. IV.D.

TABLE VI. HCl(v = 2, 1) + H - rate constants[a] determined at 296 ± 1 K.

$k_T^{1,H}$	$k_T^{2,H}$	k_{12}	k_{13}[b]	$k_{12}/k_T^{2,H}$
3.4[c]	26 ± 5	17 ± 8	9 ± 5	0.65 ± 0.15

a. Units: cm^3 $molecule^{-1}$ sec^{-1} x 10^{12}.

b. More precisely $k_{13} + k_{14} = 9 \pm 5$; $k_{14} << k_{13}$ is assumed.

c. The value (7 ± 1) x 10^{-12} cm^3 $molecule^{-1}$ sec^{-1} of Refs. 7 and 22 should be used.

TABLE VII. Vibrational relaxation of HCl by reactive atoms, $\Delta v = -1$, at 294 K.[a]

	E_{act}[b] (kcal)	σ_0[b] ($\mathring{A}^2$)	$k_{v=1}/\bar{v}$ ($\mathring{A}^2$)	$\frac{k_{v=2}}{k_{v=1}}$	$\frac{k_{v=3}}{k_{v=1}}$	$\frac{k_D}{k_H}$[c]
H	3.5	0.8	0.30	-	-	-
O	6	0.33	0.11	5.0 ± 1.3	-	-
Cl	6	3.2	1.3	4.2 ± 0.4	8 ± 2	0.62 ± 0.13
Br	16	-	0.056	5.0 ± 1.3	-	0.86 ± 0.31

a. Data for $k_{v=2}$ are from this work and Ref. 4. Other data for H and Cl are reviewed in Refs. 8 and 5, respectively. Results for O and Br are from Refs. 4 and 3, respectively.

b. Activation energy and frequency factor, $\sigma_0 = A/\bar{v}$, for thermal reaction from experiment.

c. Ratio of rate for DCl(v = 1) to that for HCl(v = 1).

Figure 1. Relative intensity data. The arrow denotes the total rate of removal of HCl($v = 2$) by Cl atoms from decay rate measurements, Table I. The intercept at 1.07×10^6 sec^{-1} torr^{-1} gives the rate of relaxation to $v = 1$, k_1. The small difference between intercept and arrow shows that the $\Delta v = 2$ relaxation to $v = 0$ is less than 10% of the total relaxation rate. The slope is fixed at the literature value of $2k_3$.

Figure 2. High temperature data corresponding to Fig. 1. The least squares slope and intercept are practically identical at the two temperatures; Table II gives the rate constants derived in density rather than pressure units.

Figure 3. Relative intensity plot. The intercept gives the rate of vibrational relaxation, k_8. The arrow indicates the total rate of loss of HCl($v = 2$) in collisions with Br. The rate of reaction to form HBr is given by the difference between the arrow and the intercept.

Figure 4. High temperature data corresponding to Fig. 3. The total loss rate, arrows, increases with temperature as does the fraction reacting. The reaction rate, k_7,increases substantially with temperature, Table IV.

Figure 5. Relative intensity plot. The slope is fixed at the literature value of $2k_3$. The intercept gives the re-

laxation rate, k_{13}. The arrow shows the value of $k_T^{2,H}$ from Table V. The large distance from intercept to arrow shows the relative importance of reaction (12).

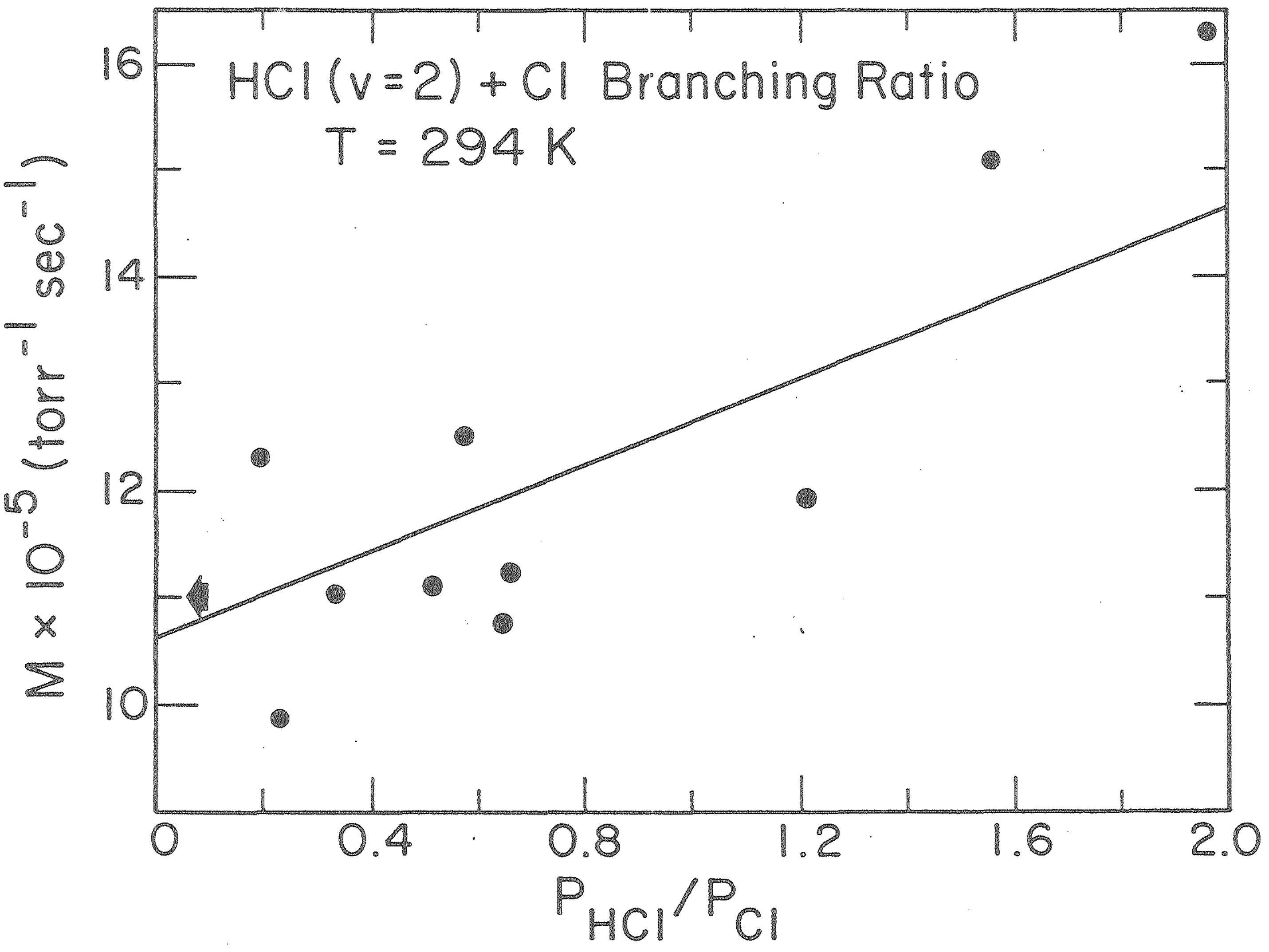
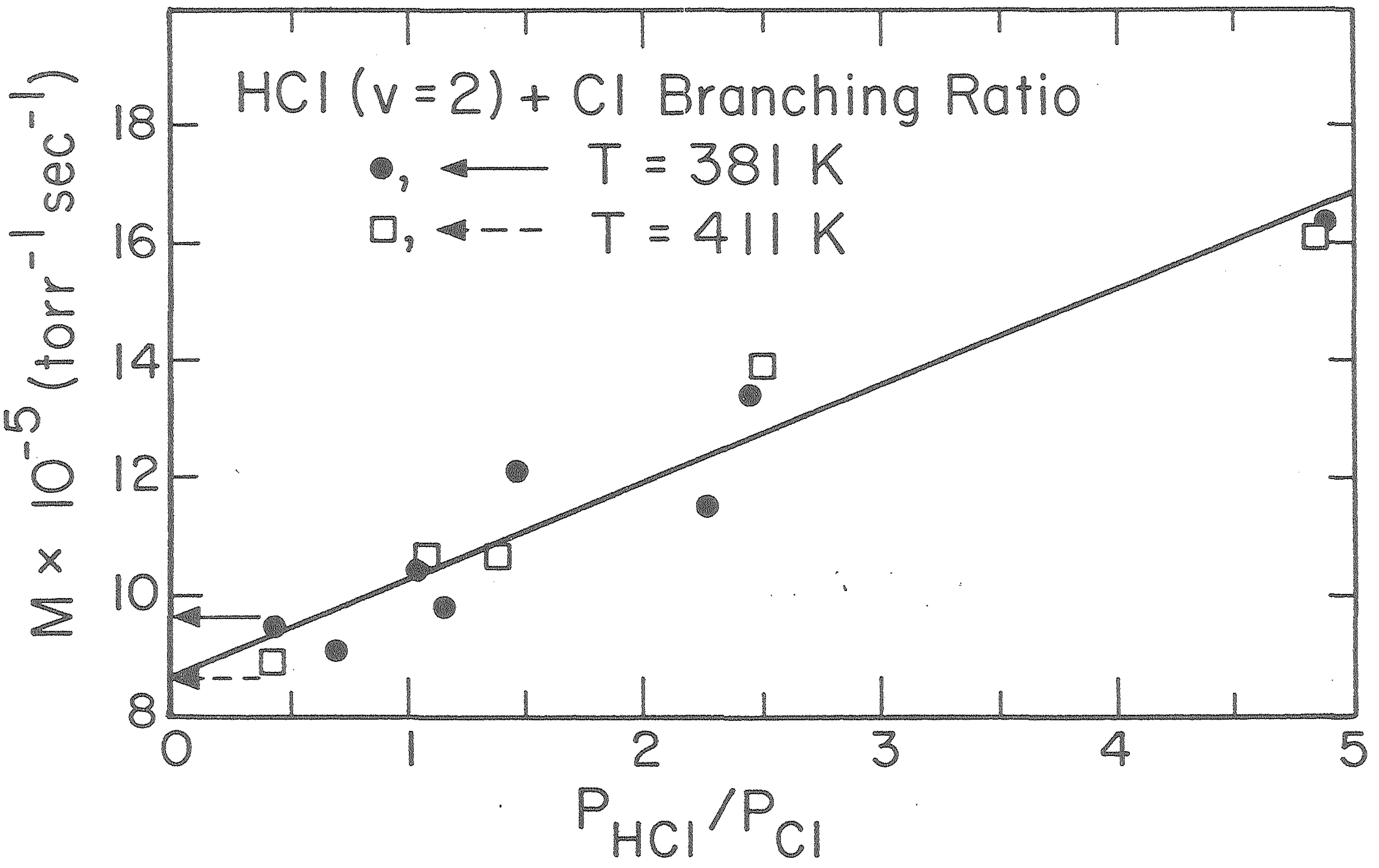

HCl (v=2) + Cl Branching Ratio
T = 294 K
M × 10^-5 (torr^-1 sec^-1)
16
14
12
10
0
0.4
0.8
1.2
1.6
2.0
P_HCl/P_Cl

Fig. 1



HCl (v = 2) + Cl Branching Ratio
●, ⟵ T = 381 K
□, ⇠ T = 411 K
M × 10^{-5} (torr^{-1} sec^{-1})
18
16
14
12
10
8
0
1
2
3
4
5
P_{HCl}/P_{Cl}

Fig. 2

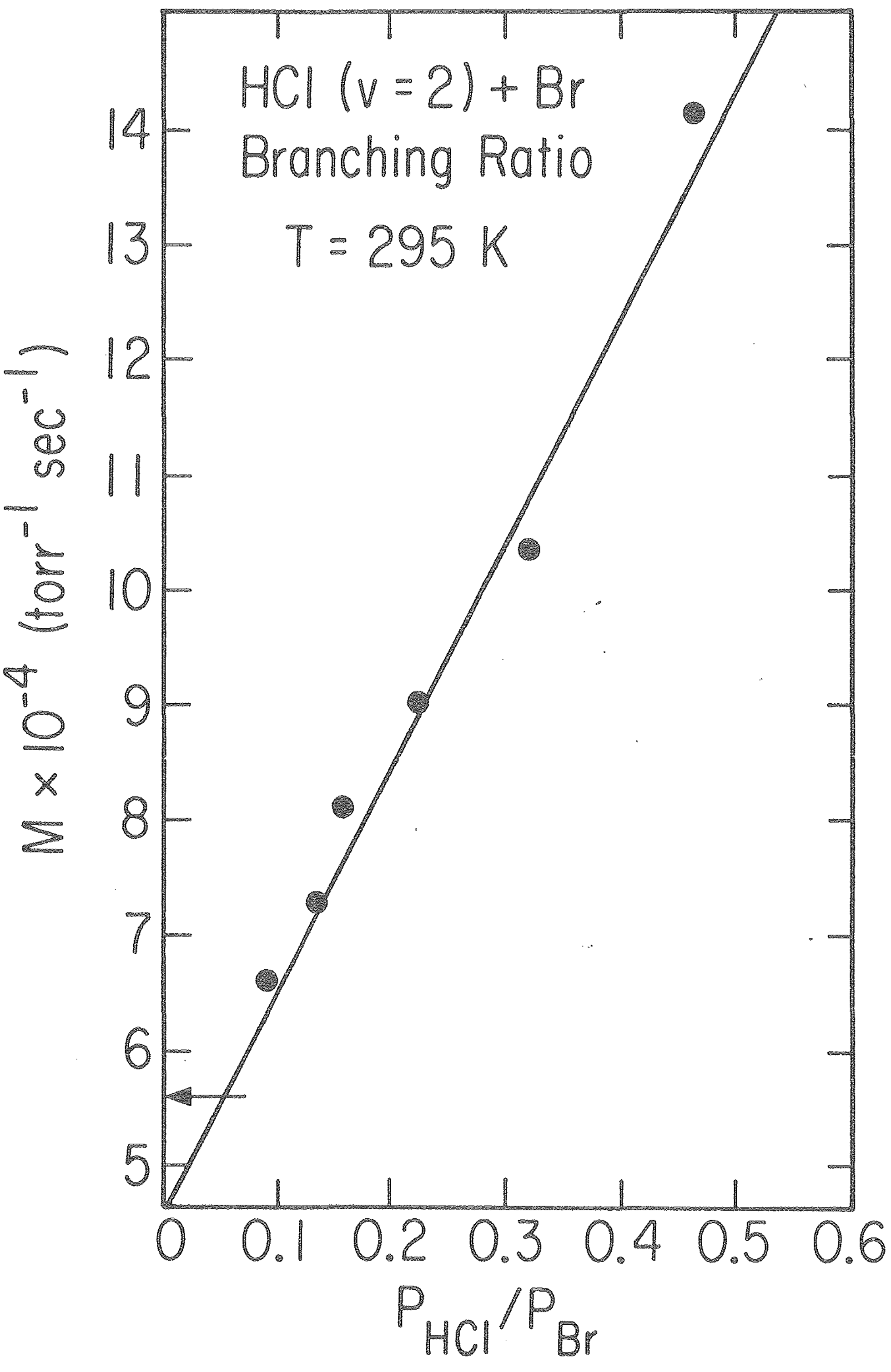

HCl (v = 2) + Br
Branching Ratio
T = 295 K
M × 10^-4 (torr^-1 sec^-1)
5
6
7
8
9
10
11
12
13
14
0
0.1
0.2
0.3
0.4
0.5
0.6
P_HCl/P_Br

Fig. 3

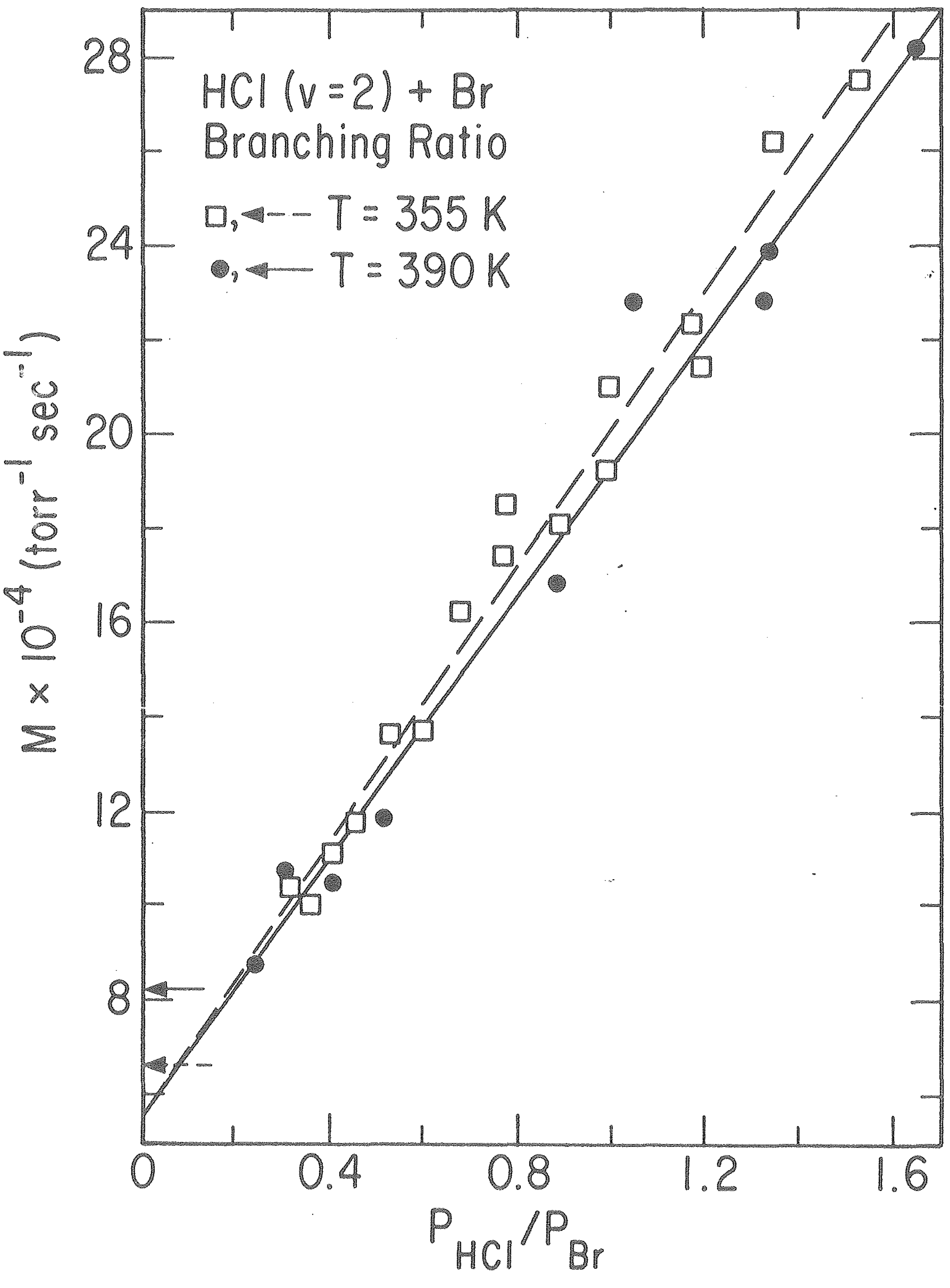

HCl (v=2) + Br
Branching Ratio
□, ◄-- T = 355 K
●, ◄— T = 390 K
M × 10^{-4} (torr^{-1} sec^{-1})
28
24
20
16
12
8
0
0.4
0.8
1.2
1.6
P_{HCl}/P_{Br}

Fig. 4

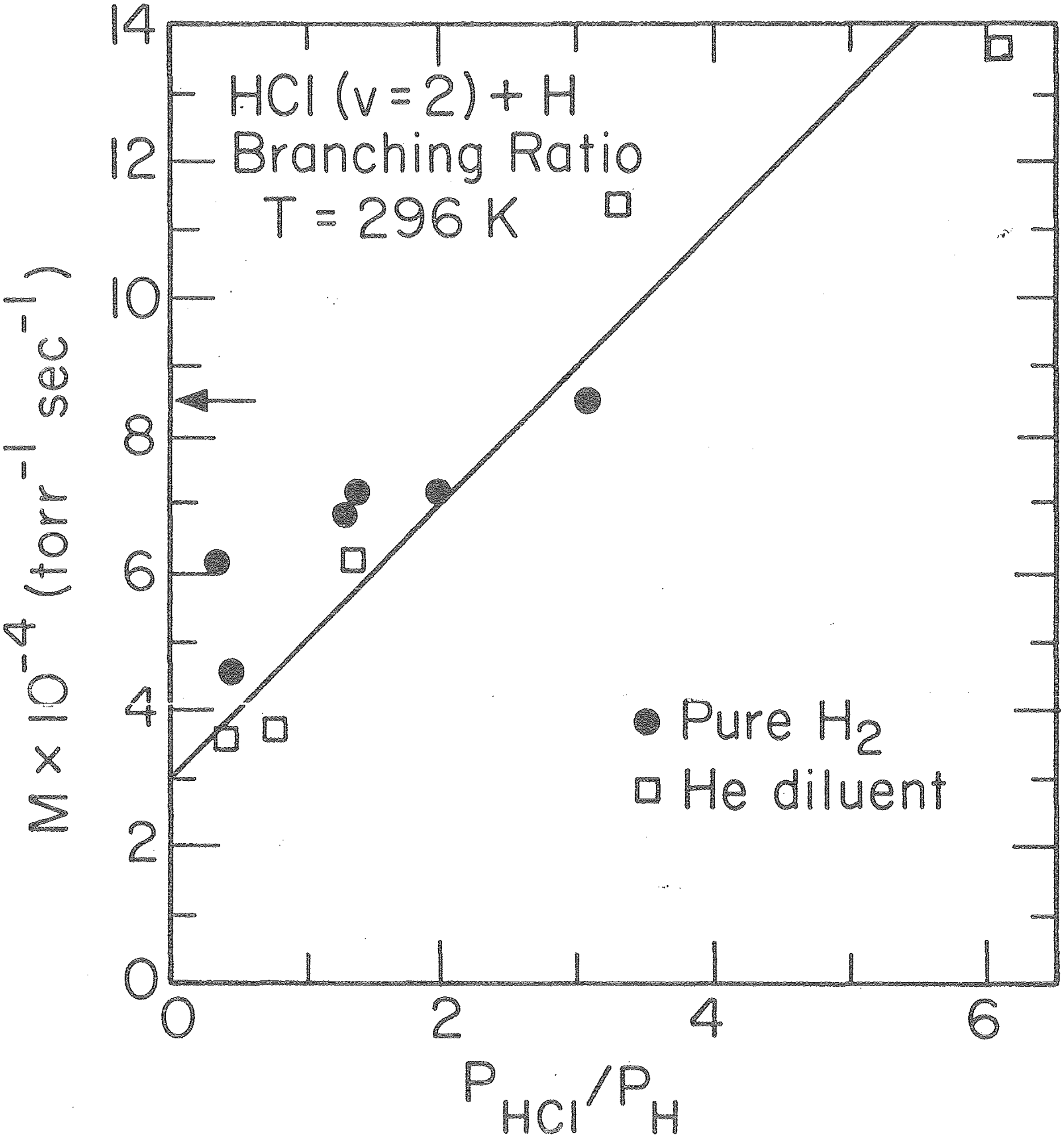

HCl (v=2) + H
Branching Ratio
T = 296 K
● Pure H_2
□ He diluent
$M \times 10^{-4}$ (torr^{-1} sec^{-1})
P_{HCl}/P_H
0
2
4
6
8
10
12
14
0
2
4
6

Fig. 5